

# Recovery of Active Materials from Spent Lithium-Ion Electrodes and Electrode Production Rejects

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## Abstract

This article describes two ways to recover valuable and ecologically critical active materials from spent lithium-ion electrodes and electrode production rejects, using the example of a system containing  $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$  (NMC) active material and a polyvinylidene fluoride (PVdF) binder. First, a physical process using thermal treatment and mechanical stressing to separate the coating from the aluminum foil is discussed. Furthermore, a wet chemical processing using the solvent n-methyl-2-pyrrolidone (NMP) is presented. Recovered coating materials from both processes were characterized by laser diffraction spectroscopy and atomic absorption spectroscopy. Additionally, recycling electrodes were produced and successfully tested in battery test cells.

## Keywords:

Electrode Recycling; Lithium-Ion-Batteries; Production Rejects

## 1 INTRODUCTION

The increasing demand of lithium-ion traction batteries implies the need for recovering active materials from spent lithium-ion-batteries (LIB) as well as from electrode production rejects to prevent a future shortage and to minimize the dependence on imported key raw materials for lithium battery production.

Lithium-ion-battery cells consist of several layers of cathodes and anodes, which are electrically isolated by an ion permeable separator to form several compartments where the electrochemical reactions can take place. These electrode-separator assemblies are embedded in a housing filled with an organic electrolyte containing a lithium rich salt. Wetting the electrodes and separators with electrolyte allows the transfer of lithium-ions between the electrodes. During the discharging process lithium-ions are transferred from the anode to the cathode, where these are inserted in a metal containing lattice structure in order to gain electrons. The electrons are transferred through the composite particle coating of the electrode towards to the current collector (anode-copper, cathode-aluminum), which itself is connected to the external electrical circuit of the battery. The described charging and discharging processes cause electrochemically, chemically and mechanically induced aging effects with a major influence on the battery performance. Since traction battery applications require extended life times of 12–15 years or of 4000 up to 5000 charge/discharge cycles these effects are of high significance.

Active materials, predominately used on the anode side, are porous graphite hosts. While lithium mixed metal oxides (e.g.  $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ , NMC) are state of the art for cathodes in the first generation of lithium-ion traction batteries. Therefore, they will be the first materials to be recycled. This research concentrates on the recycling of cathode materials since beside lithium valuable metals such as cobalt, nickel and manganese are contained. To lower the battery material investment costs material researchers try to replace these metals. A good example is lithium-iron-phosphate, which already has been established in industrial electrode production during the last two years. One has to take into account that without valuable metals lithium is the only economical concern

to develop recovering processes. Therefore a recycling process, including a hydrometallurgical processing of the coating powder, is the only pathway to recover of lithium rich products such as  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$ . These are educts for the synthesis of active materials or can be reused in secondary markets. In pure pyro-metallurgical processes lithium is lost. Selective recycling of the electrodes is of high economic interest, taken into account that

- the proportion of active materials is significantly higher in traction batteries compared to smaller consumer batteries,
- the current collectors and especially the electrochemically active materials are the components of greatest economic value in the cell,
- approximately 75% of the costs of a electric vehicle battery system are determined by the battery cell investment.

Therefore, systematic disassembling of battery systems and the following separation of the coating materials from current collector foil as well as the hydrometallurgically reprocessing of the re-won coating powder may be economically and ecologically in advance to classical pyro-metallurgical processes. This is the approach of the research project LithoRec in whose framework this research was done.

There are lots of research and development activities concerning the recycling of lithium-ion-batteries. Recent studies [1],[2],[3], and [4] give a good review about the state of the art. These processes are designed to recycle aged lithium ion secondary batteries in order to recover the valuable metals and partly to re-synthesize the active materials. In contrast to the approach of this research they are intended to recycle smaller consumer batteries. In these processes complete battery systems are destroyed mechanically or thermally to recover valuable metals subsequently by combining pyro- and hydrometallurgical processes.

The purpose is to regain materials with a minimal effort and highest quality requirements, which also allow the reuse in the field of LIB, especially directly as recovered cathode material. On the other

hand, the developed processes can result in highly concentrated suspensions, which can be used as educts for hydrometallurgical processes to recover lithium, cobalt and other purified products.

Therefore, the aim was to recover the coating powder from electrode production rejects and cycled NMC electrodes. A direct recoating of the active material applying a merely mechanical process, an alternative wet chemical recovering process or a combination of both is the main focus of this research. Basic process engineering principles were applied to separate the current collector mechanically from the particle coating. By varying the process parameters and the pretreatment of the cathodes, the coating should be separated with the highest possible yield. Additionally, the quality criteria for a use in a direct recoating process had to be achieved. At first, the particle size distribution of the re-won powder should be similar to the one of the original powder. Bigger agglomerates would result in irregularities in a re-coated electrode or would have a smaller specific surface for a following hydrometallurgical process. Whereas smaller particles would imply, that the NMC particles had been broken during the deagglomeration process. The aluminum contamination should be minimal, because aluminum can react with hydrochloric acid during the leaching step and detonating gas could degas. Furthermore, the later removal of aluminum reduces the efficiency of the hydrometallurgical step.

## 2 EXPERIMENTAL

At the LithoRec project two process paths were developed to separate the current collector from the coating in order to gain both fractions in the best purity. Both processes were developed using NMC cathode production rejects, which had not been cycled electrochemically before. The production rejects consist of a 20  $\mu\text{m}$  aluminum foil and a coating composed of NMC, a PVdF based binder and conducting agents. Later, these processes were validated by using electrodes from spent battery cells. These electrodes had been pre-dried for 10 minutes at 120  $^{\circ}\text{C}$  to evaporate the volatile fraction of the electrolyte.

### 2.1 Physical separation process

The developed physical separation process (Figure 1) can be subdivided into 4 parts: pretreatment, mechanical stress, separation, and deagglomeration. Drying for 12 hours at 150  $^{\circ}\text{C}$  or calcination at 500  $^{\circ}\text{C}$  for 15 minutes in a muffle oven turned out to be effective pretreatment steps. During the second step the pretreated production rejects were stressed in a cutting mill with a rotor peripheral speed of up to 10 m/s using a 2 mm trapezoid sieve affecting the product grit size. Afterwards the product was sieved at a mesh size of 200  $\mu\text{m}$  and the resulting fine fraction was deagglomerated in an ultra centrifugal mill with a rotor peripheral speed of up to 60 m/s. Thus, the specific surface of the resulting particles was enlarged to accelerate the following leaching process if a further hydrometallurgical treatment is carried out. Moreover, the pulverization of agglomerates results in a better coating quality regarding a direct recoating process since micron sized agglomerates bound by the PVdF binder are deagglomerated. Without this treatment agglomerates of approximately 200  $\mu\text{m}$  up to 300  $\mu\text{m}$  were observed as irregularities in the recycled coating layer. Being considered the main recycling product only the active material was balanced to quantify the separation results. Thus the fine fraction below 200  $\mu\text{m}$  was accounted as separation product.

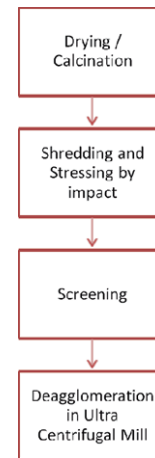


Figure 1: Physical separation process.

### 2.2 Wet chemical separation process

The wet chemical process used for this research consists of the steps presented in Figure 2. A pre-cutting step, either manual or using a cutting mill, is necessary to allow stirring of the foil-solvent mixture (step 2). In this research the pre-cut electrode rejects were stirred batch-wise in n-methyl-2-pyrrolidone (NMP) at a temperature of 90  $^{\circ}\text{C}$  for 10-20 minutes. An amount of 200 g NMP had to be used to process 100 g shredded electrode production rejects. The solving procedure was repeated six times with the same foil fraction. Afterwards, the pieces of foil were screened at 50  $\mu\text{m}$  and the fine fraction was centrifuged. The centrifugal sediment was dried at 150  $^{\circ}\text{C}$  and pulverized by an ultra centrifugal mill. Finally, the product was a powder which can be used in a direct recoating process on the one hand or processed hydro-metallurgically on the other hand.

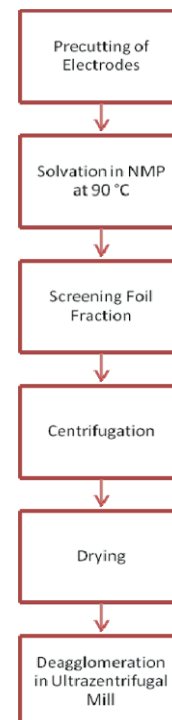


Figure 2: Wet chemical separation process.

### 2.3 Analysis

Electrode material suspensions and recycling electrodes had been prepared by dissolving the recovered materials with and without small amounts of additional binder and finally applying a standardized electrode blade coating process using NMP as solvent. The adhesive strength and the structure of the recycled electrodes were analyzed in addition to an electrochemical characterization. Furthermore, laser diffraction spectroscopy and atomic absorption spectroscopy had been applied to detect the particle size distribution of the recovered active materials and the aluminum contamination.

## 3 RESULTS AND DISCUSSION

### 3.1 Physical process

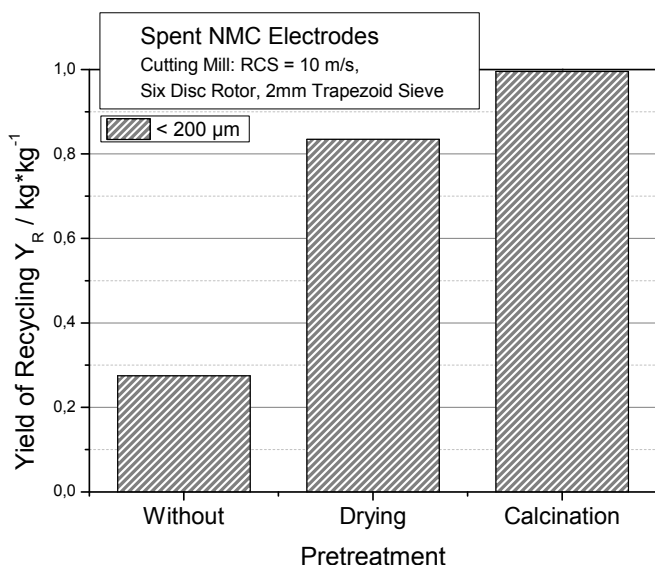


Figure 3: Influence of thermal pretreatment strategies on the Yield of Recycling of spent NMC electrodes.

The influence of different thermal strategies on the separation grade of spent NMC electrodes is shown in Figure 3. The Yield of Recycling  $Y_R$  should be defined as the mass of rewon active material, in this research study NMC, in relation to the mass of inserted active material. Processing spent electrodes only pre-dried for 10 minutes at 120 °C results in a separation yield lower than 30% of the inserted active material. Whereas drying for 12 hours at 150 °C with a loss of mass of only 0,4wt% already increases the yield to over 80wt%. This can be explained by embrittlement of the PVdF binder by some chemical reactions with the electrolyte. A calcination of the spent electrodes at 500 °C for 15 minutes before stressing them in the cutting mill leads to a yield of over 99.5wt%. According to thermogravimetric analysis the PVdF binder volatilizes at 500 °C. This lowers the adhesion between coating and foil to a minimum and thus coating material and aluminum foil can be separated easily.

The parameterization of the milling step, especially concerning the rotor circumferential speed, was carried out with production rejects not pretreated and coated on one side only. The rotor's circumferential speed (RCS) was varied from 1.2 to 10 m/s and the Yield of Recycling was determined by sieve analysis as shown in Figure 4. The fine fractions increase with the rotor's rising circumferential speed, e.g. the fraction below 200 μm shows an increase from 51% at 1.2 m/s to 78% by weight at 10 m/s. This is

caused by higher specific stress intensities with increasing rotational speed. Rotor/electrode and stator/electrode impacts become more intensive and higher fracture energy is provided. Thus, the coating layer breaks and flakes off the foil. At lower rotational speeds the stress mechanisms tend to shear and cut with lower specific stress intensities. Whereas a bottom sieve determines the maximum product size so that the foil pieces are stressed until they reach the separation size in any case.

The aluminum contamination of the fine fraction was measured by atomic absorption spectrometry. It was determined to 0,7-1% by weight. Since the contamination did not increase with higher rotational speed even higher stress intensities could be tested in further studies.

After the deagglomeration step in the ultra centrifugal mill the remaining aluminum foil pieces and agglomerates below 200 μm are pulverized from a medium particle size of 90 μm to 13 μm. Thus, the resulting powder had a particle size distribution (PSD) similar to the one of the industrial standard. Here the PSD was measured by dry dispersed laser diffraction spectrometry.

Following, electrodes were made from the recovered coating material by using a standardized NMP based electrode coating process. No supplementary binder was necessary while coating non-calcinated active materials from electrode production rejects. Whereas, for spent electrode materials an amount of 1 wt% PVdF binder had to be added in order to get a mechanical stable coating. This process yet has to be validated for calcinated active materials.

However, adhesion tests of these recycled electrodes indicated that the binder had not lost its functionality by processing.

These cathodes were electrochemically cycled in stacked pouch cells containing a recycling cathode of 25 cm<sup>2</sup>, a ceramic separator, a graphite anode and LiPF<sub>6</sub> as electrolyte. The specific capacity of the recovered NMC from production rejects measured 150 mAh/g at discharge rates of 0.5C and 125 mAh/g at discharge rates of 3C. Due to the variance in electrode preparation and in the cell assembly process these results have to be considered in the same order of magnitude like the capacity of the commercial reference material. Furthermore, the recycling cells had 87.5 % of their initial capacity after 500 cycles at charge/discharge rates of 3C/3C. In comparison, the reference electrode still had 95% of its initial capacity after 500 cycles, as shown in Figure 6.

The active material, removed from spent electrodes, had a capacity of 82 mAh/g at a cycling rate of 0.5 C and a capacity of 42 mAh/g at cycling rates of 3C. The cycle stability tests showed no further capacity reduction during the next 500 cycles. And Atomic absorption spectroscopy showed a loss of lithium of about 6 %. Additionally the capacity of 0.5 C is twice as high as the one at 3 C. Due to these facts the reason for the lower capacity of the recycled electrode is seen in structural deformation of the active material and reduced electrical conductivity of the electrode coating layer. The latter is caused by the insufficient use of the conducting agents (acetylene black and conducting graphite). Calcination of these materials and replacing them by new ones will validate this theory in further studies. Another explanation for the reduced capacity is an immobilization of lithium during the formation of the solid electrolyte interface (SEI). The SEI formation occurs during the first cycles on the anode side, where lithium is lost by the SEI film formation on the boundary layer between the electrolyte and the solid particles of the electrode. Therefore, it could be that the second delithiation of the NMC material leads to a critical amount of lithium in the lattice structure which contributes to the partial destruction of the layered structure of the metal oxide.

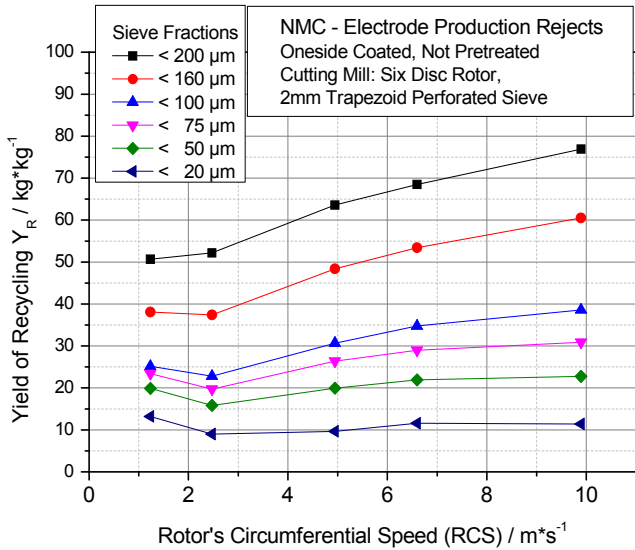


Figure 4: Influence of the Rotor Circumferential Speed on the Yield of Recycling.

3.2 Wet chemical separation process

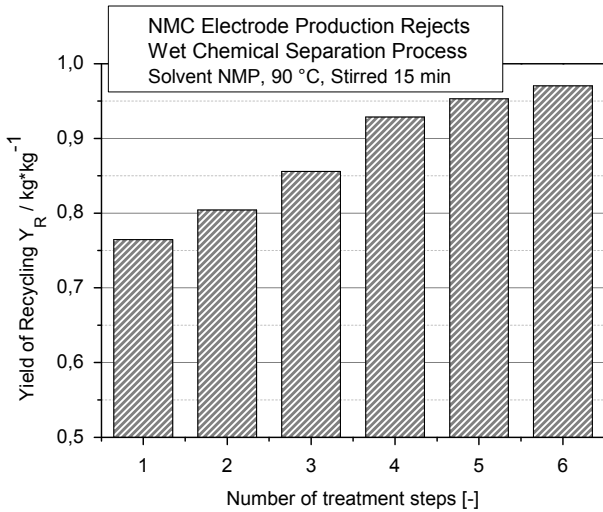


Figure 5 : Recycling yield of batchwise wet chemical separation.

As shown in Figure 5 the absolute yield of active material recycling increases with the number of treatments the foil receives. And it reaches 97wt% after the sixth treatment. The main problem of this segmented process is represented by the lack of solvent in the final phase of separation. The already detached active material partly adheres to the remaining foil when the last solvent has drained through the sieve. Thus, a process with a circulating solvent should be used to wash the remaining active material off the foil in the future.

The re-won material exhibits a PSD being similar to industrial standard after pulverization by ultra centrifugal milling. The aluminum contamination measured only 0.06 wt%, which is ten times less than in the mechanical process. This represents an

advantage for a leaching process if a hydrometallurgical processing is performed later.

As already described for the physio-mechanical process electrodes were made from the recovered coating material using a standardized electrode coating process. To coat the chemically separated powder PVdF binder was added this time in the dose of the original formula to replace the binder lost in the dilution during the recycling process.

These cathodes were built into pouch cells containing one recycling cathode, a ceramic separator, a graphite anode and LiPF<sub>6</sub> as electrolyte. Electrochemically tested, these cells still had 92.9 % of their initial capacity after 500 cycles at charge/discharge rates of 3C/3C.

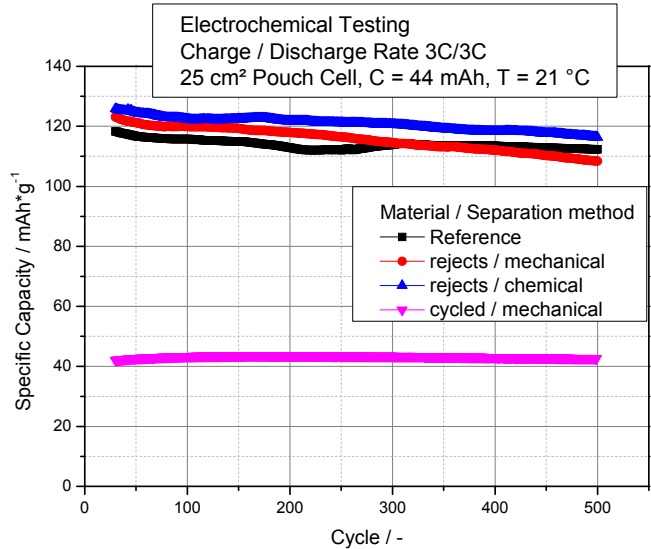


Figure 6: Electrochemical test results of re-coated NMC electrodes.

4 SUMMARY AND CONCLUSION

In this study two processes to recover active materials from spent lithium ion battery electrodes and electrode production rejects have been developed in this study. On the one hand the physical process using thermal treatment and mechanical stressing to separate the coating from the aluminum foil seems to be the easier and economically more feasible way to separate active materials from the current collector foil. This is mainly because no expensive, unhealthy and chemically aggressive solvent is needed. Further, the equipment to realize this process is simple and thus less costly. By varying the process parameters and by calcinating the cathodes in a pre-treatment step, the coating could be separated with a yield of 98 percent and higher, achieving the quality criteria for a direct recoating process.

On the other hand the main advantage of the wet chemical process is the less aluminium contamination of the product. Recycling electrodes from both processes were successfully tested in pouch cells and the first recycling electrodes made of the powder recycled by the wet chemical process had the better electrochemical cycle stability with 92.9% of the initial capacity after 500 cycles at charge/discharge rates of 3C/3C.

Considering, the discussed separation of the coating will most likely become a preparation step for a hydrometallurgical treatment, the physical separation fulfils the requirements better. Only in case of a

direct reuse of the solvent solution for re-coating the wet chemical separation has an advantage.

## 5 ACKNOWLEDGMENTS

The presented work was generated as part of the research project LithoRec, which is funded by the German Federal Environment Ministry (BMU). The authors would like to thank the BMU for the financial support.

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